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Spectrophotometric Investigations of Some Complexes of Ruthenium. II. The Ruthenium–Thiourea System[1]

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The ruthenium(IV)–thiourea system has been studied spectrophotometrically. It was found that both Ru(III) and Ru(IV) form the same blue-green complexes, $Ru(SC(NH)NH_2)_1^{+2}$ and $Ru(SC(NH)NH_2)_3$. In the reactions thiourea behaves as an acid, liberating a hydrogen ion for each molecule of thiourea which goes in the complex. At an ionic strength of 3.0, the monothiourea complex was found to have a formation constant equal to 16.3 ± 0.5, while the constant for the trithiourea complex was found to equal 5.3 ± 0.1. A method of interpretation of spectrophotometric data was developed which is applicable to two complexes of low stability.

The reaction of ruthenium(III) and ruthenium (IV) with thiourea to form a blue-green color has been reported by several investigators.[3–8] Recently it has been developed into a colorimetric method for the analysis of ruthenium.[9–11] The analytical procedure is extremely empirical, with precise limits being set on the concentrations of ruthenium, thiourea and acid present. None of the investigators has reported any study on the nature of the reaction to find out why the limits are so rigid, nor any determination of the formulas and stability constants of the complexes involved.

Preliminary investigation of the ruthenium–thiourea reaction suggested that the Ru(IV) was being reduced to Ru(III) at the expense of the complexing agent. These experiments also revealed that none of the complexes formed was very stable. The fact that ruthenium was being reduced by the thiourea meant, first, that the absorption spectrum of the uncomplexed ruthenium was unknown and, second, that at low concentration of ligand, its concentration was unknown. To keep the relative loss of thiourea insignificant, it was necessary to restrict the work to solutions in which its concentration was high. As was found in the ruthenium-thiocyanate system[12] none of the usual methods for interpreting spectrophotometric data was applicable to this particular system.

Method

In a previous paper the case of a single complex was presented.[12] This paper deals with the modifications necessary when two complexes are present. For the reactions

$$A + nB \rightleftharpoons AB_n \text{ and } AB_n + qB \rightleftharpoons AB_{n+q} \quad (1)$$

the non-thermodynamic stability constants are

$$K_1 = \frac{[AB_n]}{[A][B]^n} \text{ and } K_2 = \frac{[AB_{n+q}]}{[AB_n][B]^q} \quad (2)$$

If the total concentration of A equals c, and at equilibrium $A = c_0$, $AB_n = c_1$, and $AB_{n+q} = c_2$, then,

$$c = c_0 + c_1 + c_2 \quad (3)$$

If B is present to sufficiently large excess, so that the equilibrium concentration of B will essentially equal its total concentration, b, the equilibrium constants become

$$K_1 = c_1/c_0b^n \text{ and } K_2 = c_2/c_1b^q \quad (4)$$

If the extinction coefficient of $A = e_0$, of $AB_n = e_1$, of $AB_{n+q} = e_2$, and if B is colorless, the optical density, D, of the solution at any wave length may be written

$$D = lc_0e_0 + lc_1e_1 + lc_2e_2 \quad (5)$$

where l is the constant cell length.

By substitution for the extinction coefficients by use of the Beer–Lambert law, $d = lce$, and for the concentrations using equations (3) and (4), equation (5) may be written

$$D = \frac{(d_0/K_1b^n) + d_1 + K_2b^qd_2}{(1/K_1b^n) + 1 + K_2b^q} \quad (6)$$

After adding a sufficient excess of ligand, B, the curve obtained by plotting optical density against concentration of ligand will asymptotically approach the optical density, d_2, of the last complex. Hence it is possible to evaluate d_2 experimentally.

When virtually all of A is in the form AB_{n+q}, the contribution of A itself to the total optical density will be small, and as a first approximation may be neglected. In that case equation (6) may be reduced to

$$D = d_1 + K_2b^q(d_2 - D) \quad (7)$$

Consequently by correct choice of q, a straight line of slope K_2 and intercept d_1 may be obtained by plotting D against $b^q(d_2 - D)$. To obtain K_1 and d_0, equation (6) may be rearranged

$$D = d_0 - [(D - d_1)b^n + (D - d_2)K_2b^{n+q}]K_1 \quad (8)$$

The first approximations to d_1 and K_2 are substituted into equation (8). Plotting D against the expression in brackets with the correct choice of n gives a line of which the slope is K_1 and the intercept d_0.

Rearranging equation (6) again gives

$$D + (D - d_0)/K_1b^n = d_1 + (d_2 - D)b^qK_2 \quad (9)$$

By substituting the first approximations to d_0 and K_1, and plotting the left hand side of equation (9) against $(d_2 - D)b^q$ the second approximation to K_2 and d_1 are obtained from the slope and intercept, respectively.

This series of successive approximations, using equations (8) and (9), may be repeated as many times as necessary to obtain precise values of d_0, d_1, K_1 and K_2. The evaluation of d_1 and d_0 at all wave lengths involved gives the absorption spectra of the first complex and the uncomplexed ruthenium.

Experimental

Absorption Measurements.—A Cary automatic recording spectrophotometer was used for all optical density measurements. Matched silica cells of 2.00 cm. optical length were used. The results are expressed in terms of optical density, D, defined by the relationship, $D = \log_{10} I_0/I$, where I_0 and I are the incident and transmitted light intensities, respectively.

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[1] Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] Taken from part of the Ph.D. Thesis of Ruth Powers Yaffe, Iowa State College, 1951.

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[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944.

[10] D. D. Deford, "The Chemistry of Ruthenium," Document NP-1104, United States Atomic Energy Commission, Technical Information Division, Oak Ridge, Tennessee, 1948.

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Materials.—The preparation and standardization of the $Ru(ClO_4)_4$ and the $Ru(ClO_4)_3$ solutions have been given in a previous paper.[12] The thiourea, recrystallized Eastman Organic Chemical #497, was treated as a primary standard. The $LiClO_4$ and $HClO_4$ were from G. Frederick Smith Chemical Co. They were purified, recrystallized and standardized as necessary by standard procedures. Particular care was taken to avoid iron contamination.

Technique.—It had been shown previously[10,11] that heating was necessary to attain equilibrium within a reasonable length of time. The length of heating and the temperature used in this investigation were those selected by Deford,[10] namely, five min. in a boiling water-bath. Immediately after preparation all solutions were heated, then cooled in ice until the temperature of the solution reached 25 ± 1°. Solutions so prepared were found to be spectrophotometrically stable for only about 20 minutes. The optical density would remain constant, and then would suddenly start increasing as a turbidity appeared in solution. This turbidity was most probably due to decomposition products from the oxidation of thiourea. No way was found to avoid the turbidity, so all spectrophotometric measurements were made within 10 min. after preparation of the solutions. Furthermore, all spectrophotometric measurements were repeated a minimum of two times to check the precision of these data.

In the determination of the formulas and stability constants, in all solutions the ruthenium concentration was maintained constant at 3.351×10^{-4} *M*, with the perchloric acid concentration constant at 0.254 *M*, and the ionic strength constant at 3.0. Solutions were prepared by mixing necessary quantities of a solution of $Ru(ClO_4)_4$ and a freshly prepared solution of thiourea to give the final concentrations. Equilibrium was attained by the previously described heating and cooling procedure. More than thirty-five solutions which contained ratios of thiourea to ruthenium from 3.33 to 9000 were so prepared and scanned.

Discussion

A typical constant wave length plot of the optical density as a function of the thiourea to ruthenium ratio is given in Fig. 1. This figure shows clearly that the optical density of the solution does not change for ratios greater than 2000 (the line labeled d_3 in Fig. 1). Hence the absorption spectrum of the last complex is known from experimental data. Absorption spectra of this complex are given in Fig. 2, from which it may be seen that the complex obeys Beer's law.

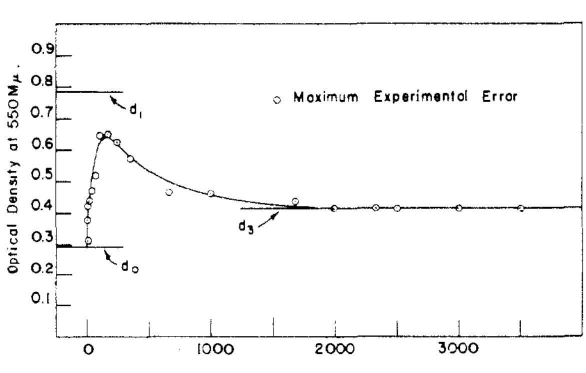


Fig. 1.—Optical densities at 550 mμ of various solutions with excess thiourea present: [Ru] = 3.351×10^{-4} *M*; $[H^+] = 0.254$ *M*; $\mu = 3.0$; cell length = 2.00 cm.; circles, experimental points; curve, calculated on the basis of $Ru(th)_1^{+2}$ and $Ru(th)_3$.

From Fig. 1, it is noted that the optical density *versus* ratio curve goes through a maximum. It is apparent that there must be at least two complexes present, the last complex, and another with a higher extinction coefficient. The simplest assumption consistent with fact was made, namely, that only two complexes were present.

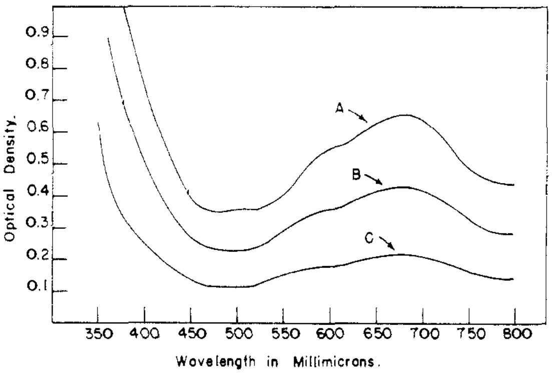


Fig. 2.—Absorption spectra of $Ru(th)_3$: $[H^+] = 0.254$ *M*; $\mu = 3.0$; cell length = 2.00 cm.; A, [Ru] = 3.351×10^{-4} *M*; B, [Ru] = 2.234×10^{-4} *M*; C, [Ru] = 1.117×10^{-4} *M*.

By making this assumption the following equations may be written

$$Ru^{+3} + n\text{Hth} \rightleftharpoons Ru(th)_n^{3-n} + nH^+$$

$$Ru(th)_n^{3-n} + q\text{Hth} \rightleftharpoons Ru(th)_{n+q}^{3-n-q} + qH^+$$

where Hth is used as an abbreviation for thiourea.

As a special case of equation (6) the relation may be formulated

$$D = \frac{\dfrac{d_0[H^+]^n}{K_n[\text{Hth}]^n} + d_1 + \dfrac{K_{n+q}[\text{Hth}]^q d_3}{[H^+]^q}}{\dfrac{[H_+]^n}{K_n[\text{Hth}]^n} + 1 + \dfrac{K_{n+q}[\text{Hth}]^q}{[H^+]^q}}$$

K_n and K_{n+q} are the formation constants for $Ru(th)_n^{3-n}$ and $Ru(th)_{n+q}^{3-n-q}$, respectively, and d_0, d_1 and d_3 are the optical densities of the uncomplexed ruthenium, the first complex, $Ru(th)_n^{3-n}$, and the second complex, $Ru(th)_{n+q}^{3-n-q}$, respectively. In the analysis of the system this equation was used in a series of successive approximations. Values of *q* equal to one, one-half, three-halves, three and four were tried unsuccessfully. Only a choice of *q* equal to two made the data interpretable. Similarly, values of *n* equal to one-half, three-halves, two, three and four were unacceptable, while a choice of *n* equal to one proved satisfactory. Thus the reactions should be written

$$Ru^{+3} + \text{Hth} \rightleftharpoons Ru(th)_1^{+2} + H^+$$

$$Ru(th)_1^{+2} + 2\text{Hth} \rightleftharpoons Ru(th)_3 + 2H^+$$

The equilibrium constants are

$$K_1 = \frac{[Ru(th)_1^{+2}][H^+]}{[Ru^{+3}][\text{Hth}]}, \text{ and } K_3 = \frac{[Ru(th)_3][H^+]^2}{[Ru(th)_1^{+2}][\text{Hth}]^2}$$

Three successive approximations were carried out in the evaluation of k_1 and k_3. The results are summarized in Table I.

TABLE I

SUMMARY OF SUCCESSIVE APPROXIMATIONS TO K_1 AND K_3

Approximation	K_1	K_3
1	18 ± 2	4.6 ± 0.3
2	16.3 ± 0.7	5.2 ± .2
3	16.3 ± .5	5.3 ± .1

In each approximation, values of the equilibrium constant, K_3, were calculated at 10-mμ intervals over the spectrum from 400 to 550 mμ and then averaged. Similarly, K_1 was calculated at 10-mμ intervals over the spectrum from 500 to 700 mμ, and then averaged.

By use of the final values found for the equilibrium constants, K_1 and K_3, the absorption spectra of the first complex and the uncomplexed ruthenium were calculated. The absorption spectrum of the first complex, $Ru(th)_1^{+2}$, is given in Fig. 3. The absorption spectrum of the uncomplexed ruthenium was essentially that of $Ru(ClO_4)_3$, and differed from the spectrum of $Ru(ClO_4)_4$ sufficiently to justify the conclusion that the ruthenium is in the III state in the complex.

By use of the calculated equilibrium constants, K_1 and K_3, and the calculated values, d_1 and d_0, together with the experimental value, d_3, the optical density curve as a function of the thiourea to ruthenium ratio was calculated at 550 mμ. This is the curve drawn through the experimental points in Fig. 1.

Although the equations and equilibrium constants in the ruthenium–thiourea system have been written as a function of the hydrogen ion, this assumption must be proven. To test this dependence, the above procedure was repeated at 0.508 *M* instead of 0.254 *M* $HClO_4$. This work was not done in as great detail since the nature of the reaction was now known. Only the first approximation was carried out in the calculations. This was compared to the first approximation calculations at the lower acidity. The results of these calculations are summarized in Table II.

TABLE II

COMPARISON OF FIRST APPROXIMATIONS TO K_1 AND K_3 IN 0.254 AND 0.508 *M* $HClO_4$

$[HClO_4]$, *M*	$K_1 = \frac{[Ru(th)_1^{+2}][H^+]}{[Ru^{+3}][Hth]}$	$K_3 = \frac{[Ru(th)_3][H^+]^2}{[Ru(th)_1^{+2}][Hth]^2}$
A. Assuming hydrogen ion dependence		
0.254	18 ± 2	4.6 ± 0.3
.508	20 ± 4	4.6 ± .8
$[HClO_4]$, *M*	$K_1 = \frac{[Ru(Hth)_1^{+3}]}{[Ru^{+3}][Hth]}$	$K_3 = \frac{[Ru(Hth)_3^{+3}]}{[Ru(Hth)_1^{+2}[Hth]^2}$
B. Not assuming hydrogen ion dependence		
0.254	71 ± 8	72 ± 5
.508	39 ± 8	18 ± 3

From Table II it is seen that the assumption of hydrogen ion dependence gives agreement in both equilibrium constants at the two acidities, whereas the assumption of no dependence does not. Therefore it must be concluded that thiourea is behaving as an acid, with each molecule of thiourea releasing one proton.

The possibility that the reactions are the following rather than those given previously has also been considered

$$Ru^{+3} + Hth + H_2O \rightleftharpoons Ru(Hth)OH^{+2} + H^+$$

$$Ru(Hth)OH^{+2} + 2Hth + 2H_2O \rightleftharpoons Ru(Hth)_3(OH)_3 + 2H^+$$

However, it does not seem likely that hydrolysis would be an important part of the reactions at these acidities. It seems even less likely that the complexed species would be more highly hydrolyzed than the uncomplexed one. If this were to account for the observed constancy of the *K*'s over a twofold change in hydrogen ion concentration, the hydrolysis of the complexed species would have to be essentially complete to the forms shown in the equations, while the hydrolysis of the uncomplexed ruthenium would have to be negligible. As another argument, the second complex is known to be partially extractable into a few organic solvents, a behavior one would expect on the basis of the simple complex, $Ru(th)_3$, but not in the hydrolyzed complex, $Ru(Hth)_3(OH)_3$. If chelation occurs the hydrolyzed form of the second complex would be excluded since all six coördination positions would be occupied.

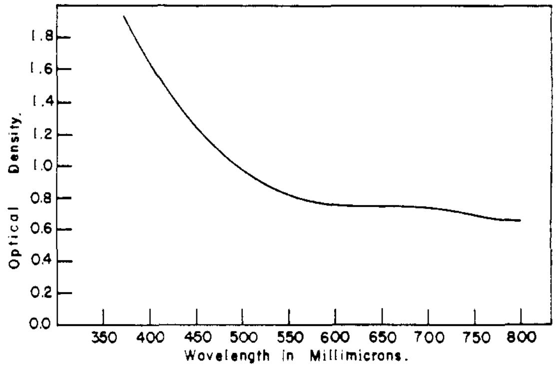
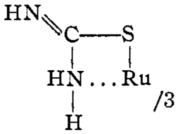


Fig. 3.—Calculated absorption spectrum of $Ru(th)_1^{+2}$: [Ru] = 3.351 × 10^{-4} *M;* $[H^+]$ = 0.254 *M;* μ = 3.0; cell length = 2.00 cm.

If the ruthenium–thiourea complexes involve chelate rings, these rings would have only four members, and hence would not be expected to be very stable. However four-membered rings containing C–N–S–metal are known,[13] and it seems quite reasonable that the ruthenium–thiourea complexes are of this type (I).


(I)

Since $Ru(ClO_4)_3$ is not stable at room temperature, no extensive work was carried out using it. However Ru(III) in the presence of sufficient excess of thiourea to complex all of the ruthenium as $Ru(th)_3$ gave an absorption spectrum identical with that obtained when Ru(IV) was used.

Magnetic susceptibility measurements, made by Dr. C. V. Banks and Mr. Roy W. Vander Haar of the analytical chemistry division of the Ames Laboratory, demonstrated that the $Ru(th)_3$ complex was paramagnetic. In order that all of the ruthenium would be in this form a large excess of thiourea was added to the solution. This meant that it was necessary to detect 0.1 g. of paramagnetic material in 1100 g. of diamagnetic material. After subtracting the diamagnetic contributions to the total susceptibility, the net value for the

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(13) F. J. Welcher, "Organic Analytical Reagents," Volume I, Chapter IV; Volume IV, Chapter V; D. Van Nostrand Co., New York, N. Y., 1948.

gram susceptibility of the complex was +3 ± 1.5 c.g.s. units/g. at 20°. This is sufficiently positive to indicate the undoubted paramagnetic nature of the complex, and if multiplied by the molecular weight of $Ru(th)_3$ of 331, gives a molar susceptibility of 1000 ± 500 c.g.s.u./mole. Since the contribution of one unshared electron would be about 1300, and since Ru(III) in covalent compounds has one unshared electron, within the experimental error this shows that the ruthenium in the complex is in the III state. Ru(IV) must be excluded since it has an even number of electrons and would hardly be expected to have one unpaired electron.

Conclusion

Ruthenium(III) and ruthenium(IV) perchlorate react with thiourea Hth, to form two blue-green complexes, $Ru(th)_1^{+2}$ and $Ru(th)_3$. The complexing agent behaves as an acid and each molecule of thiourea releases a proton. At an ionic strength of 3.0, the monothiourea complex was found to have a formation constant, K_1, equal to 16.3 ± 0.5, while the constant K_3 for the trithiourea complex was found to equal 5.3 ± 0.1. No evidence was found for the dithiourea complex, $Ru(th)_2^+$.

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Absolute Verdet Constants for Water over a Range of Temperatures and Visible Wave Lengths

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The purpose of this paper is to present new absolute values for the Verdet Constant of water over a range of temperatures and visible wave lengths. Based upon measurements of the magnetic rotation of water and measurements of the field strength of the solenoid employed, these values have been calculated with uncertainties of ±0.05%. The results obtained serve to define more specifically this important constant for water and to answer directly certain questions that have been raised in the literature during the past years.

I. Introduction

When a beam of plane polarized monochromatic light is passed through any transparent isotropic liquid or solid, placed in a magnetic field parallel to the lines of force of the field, the plane of vibration of the light beam is rotated through a definite angle. This phenomenon is known as the Faraday effect. If R is the total angle of rotation in minutes, l the length of the substance in centimeters through which the light beam passes, H the magnetic field strength in gauss, θ the angle between the direction of the magnetic field and the light path, and V the proportionality constant, then

$$R = V \times l \times H \times \cos \theta$$

It has been found that every substance has a characteristic value for the proportionality term, V, and this has been named the Verdet constant. V varies with wave length and temperature in a manner analogous to the refractive index of substances. A more useful term for the identification of molecular species and characteristic functional groups is the molecular Verdet constant, $\mathbf{V}$, which is the Verdet constant multiplied by the molecular weight and divided by the density of the substance.

For some time there has been an increasing interest in the Faraday effect from both the experimental and the theoretical standpoint. To date, unfortunately, there has not been good correlation between theory and experiment. The lack of precise, absolute values for the Verdet constants for various pure substances has been mainly responsible for this discrepancy. The need, then, for precise values of absolute Verdet constants to overcome this limitation has long been recognized.

Water is by far the most widely studied substance from the standpoint of the Faraday effect. At present, however, there is still uncertainty in the Verdet constants for this important substance. Current values given in the literature refer mainly to a single wave length and temperature, and there is some discordancy among them. This is largely due to inaccuracies of the method of obtaining the magnetic field strength. For example, the most recently published value for the absolute Verdet constant for water[2] was obtained from a calculated, rather than an experimentally determined value of the field strength of the solenoid employed.

In view of this it was felt that the absolute Verdet constants for water should be redetermined over a range of temperatures and wave lengths. It is the purpose of this paper, therefore, to present new absolute Verdet constants for water using a precision Faraday effect apparatus[3] and an experimentally determined magnetic field strength.

II. Experimental

Four different water samples were employed for the measurements; three were triple-distilled and the fourth was distilled once. Sample 1 was ordinary tap water distilled once by a Vigreux column. Samples 2, 3 and 4 were distilled in a Barnes Laboratory still and then distilled from alkaline permanganate in a Vigreux column. This distillate was again distilled from the Vigreux column. The criterion of purity used was the refractive index which was measured on a Bausch and Lomb precision refractometer. At 20°, four different water samples varied by only 0.00001 with the literature values[4] at 589 mμ.

Values of the magnetic field strength of the Faraday solenoid, at points over a range of 14 cm. along the axis on either side of the center, were obtained from measurements

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(1) The data presented were submitted in partial fulfillment of the requirements of the Ph.D. degree at the University of Connecticut.

(2) R. deMallemann, P. Gabiano and F. Guillaume, *J. phys. radium*, [8] **5**, 41 (1944); R. deMallemann, P. Gabiano and F. Suhner, *Compt. rend.*, **202**, 837 (1936).

(3) Samuel Steingiser, George J. Rosenblit, Robert L. Custer and Chas. E. Waring, *Rev. Sci. Instruments*, **21**, 109 (1950).

(4) Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1940, pp. 200-202.